Evaluation of Methods For the Assay of Radium-228 in Water
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Evaluation of Methods For the Assay of Radium-228 in Water

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EVALUATION OF METHODS FOR THE ASSAY OF RADIUM-228 IN WATER

by

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The technical literature from 1967 to May 1980 was searched for methods for assaying radium-228 in water. These methods were evaluated for their suitability as potential EPA reference methods for drinking water assays. We suggest the present EPA reference method (Krieger, 1976) be retained but improved, and a second method (McCurdy and Mellor, 1979), which employs $\beta-\gamma$ coincidence counting, be added. Included in this report is a table that lists the principal features of 17 methods for radium-228 assays.

Key words: Analysis; assay; evaluation; radioactivity; radiochemistry; radium-228; reference method; water.

Introduction

Radium-228 is a radionuclide hazardous to human health because, like radium-226, it is incorporated into the skeleton and has a long biological residence time. Radium-228 is ingested primarily by the drinking of water. It has been found to occur in higher concentrations than $^{226}$Ra in water in contact with some geologic formations in the United States (Johnson, 1971; Michel and Moore, 1980) and in Brazil (Hainberger, 1974). Radium-228 is difficult to assay accurately, especially at low concentrations, because it emits only very low-energy conversion electrons (less than 6 keV) and low-energy beta particles (10 keV average energy). Other isotopes of radium or their daughters cannot readily be added to samples as tracers for measuring the chemical yields of assays because: 1) they are also likely to be present in the water, particularly $^{224}$Ra and $^{226}$Ra, or 2) they are themselves inconvenient to prepare and assay, as in the cases of $^{223}$Ra and $^{225}$Ra.
The U. S. Environmental Protection Agency has regulations which set limits on the concentrations of radionuclides, including $^{228}$Ra, in drinking water (EPA, 1976), and which specify approved assay methods. The EPA reference method for $^{228}$Ra (Krieger, 1976) is based on a U.S. Geological Survey method (Johnson, 1971), which was also recommended by the World Health Organization (Lund, 1976). In addition, the U.S. Food and Drug Administration (FDA, 1979) has regulations pertaining to radionuclides in bottled water, modelled on the EPA regulations. Other methods for the low-level assay of $^{228}$Ra are available, but each of them, as well as the present reference method, has one or more deficiencies for use in monitoring.

All assay methods for radionuclides should have sufficient and demonstrated precision, accuracy, and sensitivity to meet the purposes of the assay. With the possible exception of simple screening tests, such as "gross α" measurements, all radiochemical methods also should incorporate steps for determining the chemical yield.

There are additional desirable features that should be present in an ideal monitoring method. The method should be "rugged", which means it will perform well under less than ideal conditions. It should provide results without requiring a long wait for the ingrowth or decay of a radionuclide, and it should be suitable for use with large numbers of samples; that is, it should have relatively low labor and supply costs.

The Quality Assurance Division in the Environmental Monitoring Systems Laboratory of the EPA, Las Vegas, requested the NBS Radioactivity Group, Nuclear Radiation Division, to survey the literature for $^{228}$Ra assay methods and evaluate their suitability as potential EPA reference methods.
Survey of Literature

Nuclear Science Abstracts was searched from 1967 until its termination in 1977. Then, the Energy Data Base was searched from 1977 through May 1980. Also, Chemical Abstracts was searched from 1968 through May 1980. References cited in the relevant papers found in these searches led to other papers dating from approximately 1960.

There are only a few papers giving methods for assaying $^{228}$Ra in water and the results of such measurements. Many of the available papers deal with seawater rather than fresh water. The pertinent aspects of the methods are set forth in Table 1 in alphabetical order of author. Some of these publications also deal with $^{226}$Ra assays, and salient features of these methods are included in Table 1. Papers concerned only with $^{226}$Ra assays are not included.

Also in Table 1 are $^{228}$Ra assay procedures found during the search that are for other types of samples, such as soil. The latter methods usually can be adapted to the assay of water samples, and some contain useful techniques not exploited in the water-assay procedures. Reports of investigations using previously published $^{228}$Ra assay procedures are excluded.

Evaluation of Methods

Most of the following discussion further explains important points made in Table 1. Nearly all the assay methods separate and purify $^{228}$Ac and count beta particles emitted in its decay. The method of McCurdy and Mellor (1979) is unique in that the $^{228}$Ac is not separated from its $^{228}$Ra parent for counting. Thus, $^{228}$Ac can be counted as long as desired or recounted days later.
without performing additional radiochemistry on the sample. A few procedures use the detection of radiations emitted by later members in the $^{228}\text{Ac}$ decay series, including $^{228}\text{Th}$, $^{224}\text{Ra}$, and even $^{212}\text{Pb}$ from de-emanated $^{220}\text{Rn}$. Only the method of Tomza (1977) uses liquid-scintillation counting.

The assay methods listed in Table 1 appear to have the sensitivity required by the EPA drinking water regulations (EPA, 1976), with the apparent exceptions of those of Iyer et al. (1966) and Baretta and Feldman (1961). There is some evidence that at low $^{228}\text{Ra}$ concentrations a method for counting alpha particles from the decay of $^{228}\text{Th}$ has better precision than one for counting beta particles from the decay of $^{228}\text{Ac}$ (Knauss et al., 1978), but the time required for $^{228}\text{Th}$ ingrowth is much longer than that for $^{228}\text{Ac}$.

The methods in Table 1 lacking a provision for determining the chemical yield for each sample processed are those of Humphrey et al. (1975), Johns et al. (1979), Kuchta et al. (1976), MacKenzie et al. (1979), Percival and Martin (1974), Petrow et al. (1964), Sakanoue et al. (1973), and Tomza (1977). This is also true of procedures of Barratta and Feldman (1961), and of Kahlos and Asikainen (1973), but both could readily be modified for gravimetric determination of chemical yields. Some of the methods which do provide a chemical yield, however, require long waiting times (see below).

Four of the methods use radioactive tracers to measure chemical yields: Kaufman et al. (1973), Koide and Bruland (1975), Michel and Moore (1980), and Smith and Mercer (1970). Because the present EPA reference methods for radio-nuclides other than tritium do not require radioactive tracers (Krieger, 1976), it was assumed they are to be avoided when another yield-measuring technique
is available. It should be noted that the chemical yield is incorrectly calculated in the reference method for $^{228}$Ra (Krieger, 1976). Any loss of sample in steps 13 and 14 is counted twice. The Ba(Ra)SO$_4$ precipitate at the end of step 11 should be weighed, rather than in step 25 as stated.

The waiting periods in the methods given in Table 1 for ingrowth or decay of radionuclides during an assay can be divided into three groups: less than two full days, two days to 30 days, and greater than 30 days. Waiting periods include time for the ingrowth of $^{222}$Rn for those procedures where assays of $^{226}$Ra are an integral part of the $^{228}$Ra assays. The short-time procedures in the first group are Raratta and Feldman (1961), Humphrey et al. (1975), Iyer et al. (1966), Krieger (1976), McCurdy and Mellor (1979), Percival and Martin (1974), and Petrow et al. (1964). Methods with waiting periods of between two and 30 days are Johns et al. (1979), Kahlos and Asikainen (1973), Koide and Bruland (1975), and Smith and Mercer (1970) (via $^{228}$Ac). Methods requiring waiting times of longer than 30 days are Kaufman et al. (1973), Kuchta et al. (1976), MacKenzie et al. (1979), Michel and Moore (1980), Sakanoue et al. (1973), Smith and Mercer (1970) (via $^{228}$Th), and Tomza (1977).

The methods of Kuchta et al. (1976) and Tomza (1977) would have waiting times of only two to 30 days if $^{224}$Ra were known to be in equilibrium with $^{228}$Ra, but this condition would probably be rare for drinking water. Finally, the waiting period in the procedure of MacKenzie et al. (1979) could also be reduced to between two and 30 days if the more volatile beta-particle-emitting progeny of $^{228}$Ac could be flamed off a
source evaporated on a stainless steel planchet with no accompanying loss of $^{228}\text{Ac}$ (compare with Koide and Bruland (1975)).

A potential problem confronting the methods which assay $^{228}\text{Ra}$ via $^{228}\text{Ac}$ is the presence of radioisotopes of the rare-earth elements or those with similar chemical properties, especially $^{90}\text{Y}$, daughter of $^{90}\text{Sr}$. Some of the procedures have one or more steps designed to reduce such contamination, and the $\beta-\gamma$ coincidence counting technique of McCurdy and Mellor (1979) is not affected by $^{90}\text{Y}$. A recent interlaboratory assay exercise, with a water test sample that had $^{90}\text{Sr}-^{90}\text{Y}$ added, indicated that the present EPA reference method does not adequately remove $^{90}\text{Y}$ from $^{228}\text{Ac}$ (Whittaker, 1980).

The Y or La compound chosen as the carrier for Ac should be checked for radiochemical purity before use, because it may be a significant source of beta activity (Johnson, 1971). Such a warning should be added to the reference method.

It is difficult to assess the "ruggedness" of an analytical method from just a literature survey. In general, the less complex an assay procedure is, the better chance of its being "rugged". However, some of the simpler procedures in Table 1 are without a means for measuring chemical yields.

The "special apparatus" columns in the table list items needed for each method that are judged not likely to be present in the usual water-analysis laboratory. Some of these items, such as the $\beta-\gamma$ coincidence-counting system of McCurdy and Mellor (1979), are a significant expense.
Conclusions

Most of the $^{228}$Ra assay methods in Table 1 are eliminated from consideration as an EPA reference method by applying the criteria discussed earlier: adequate sensitivity, yield determination without radioactive tracers, and a waiting time for ingrowth or decay of radionuclides in the sample of no more than 30 days. The methods meeting these criteria, but with the reservation already noted about each, are Kahlos and Asikainen (1973), Krieger (1976) and McCurdy and Mellor (1979). The first of these three would be eliminated if the requirement of a waiting period for ingrowth or decay of no more than two days were imposed. It is possible that Iyer et al. (1966) and Barratta and Feldman (1961) are sufficiently sensitive, but multilaboratory studies would be necessary to demonstrate this.

It is suggested that the EPA keep Krieger (1976) as a reference method but improve its decontamination factor for $^{90}$Y and correct its chemical yield calculation. It is also suggested that McCurdy and Mellor (1979) be added as a second reference method. The two procedures complement each other. The first uses radiation-detection systems which most laboratories that assay for radionuclides in water are likely to have, but it requires a considerable amount of labor to process samples. The second requires most laboratories to purchase a new radiation-detection system, but the labor to process samples is definitely less.


Michel, J., and W.S. Moore (1980), "226Ra and 228Ra content of groundwater in fall line aquifers", Health Physics, 38, 663.


The following papers were obtained too late to include in Table 1. They do not alter the conclusions of this report because none is suitable as a reference method for radium-228 assays. The radiochemical section of the Herment paper deals with the production of radium-228. Neither of the other two papers has a way to determine the chemical yield of an assay.


Table 1. Comparison of Major Features of Methods for the Assay of Radium-228 in Water
<table>
<thead>
<tr>
<th>Reference</th>
<th>Intended Use</th>
<th>Sample Size</th>
<th>Preliminaries</th>
<th>Ra Separation</th>
<th>Purification</th>
<th>Final Form</th>
<th>Yielded By</th>
<th>Counted By</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baratta and Feldman (1961)</td>
<td>Assay of Ac in U kill effluents and natural waters</td>
<td>1 liter</td>
<td>Ac pptd. with La (12 mg) by HF</td>
<td>On Ba(NO$_3$)$_2$ in 75% HNO$_3$; $^6$Ra soln.</td>
<td>Solution evaporated on stainless steel planchet, planchet flamed</td>
<td>Nothing</td>
<td>Frisch-grid ionization chamber of 4.78 MeV, with PHA</td>
<td></td>
</tr>
<tr>
<td>Humble et al. (1975)</td>
<td>$^{228}$Ra and $^{228}$Ra in effluent solutions with high $^{40}$K concentration</td>
<td>250 ml</td>
<td>None</td>
<td>On 100 ng of Ba pptd. as Ba(NO$_3$)$_2$; Ba weighed before and after Ra separation</td>
<td>Water and Microsorb filters; none; soil and glass-fiber filters; reagent on BaSO$_4$; Dissolve ppt. in alkaline EDTA-solution, reagent sulfates at pH 4.5 with acetic acid</td>
<td>Water and Microsorb filters; OPTA complex in acetic acid; others: chloride solution</td>
<td>Nothing</td>
<td>Ra de-emanated into scintillation chamber after 30 days ingrowth. Counting begun 4.5 h after transfer</td>
</tr>
<tr>
<td>Iyer et al. (1966)</td>
<td>Assay of natural radioactivity in ground water</td>
<td>2 to 5 g</td>
<td>Digest with H$_2$SO$_4$ in Pt dish and fuse with Na$_2$CO$_3$ and K$_2$CO$_3$; Dissolve in HNO$_3$</td>
<td>On 1000 mg of Ba pptd. as Ba(NO$_3$)$_2$; Ba weighed before and after Ra separation</td>
<td>Water, air filters: coppt. on PbSO$_4$; sol. coppt. on BaSO$_4$</td>
<td>Water and Microsorb filters; OPTA complex in acetic acid; others: chloride solution</td>
<td>Nothing</td>
<td>Ra de-emanated into scintillation chamber after 30 days ingrowth. Counting begun 4.5 h after transfer</td>
</tr>
<tr>
<td>Johns et al. (1979)</td>
<td>Assay of natural radioactivity in sea water</td>
<td>1 liter</td>
<td>Citric acid and NH$_4$OH added to filtered sample, then Ba and Pb carriers</td>
<td>Mixed sulfates pptd. with H$_2$SO$_4$</td>
<td>Dissolve ppt. in alkaline EDTA-solution, reagent sulfates at pH 4.5 with acetic acid</td>
<td>25% Ag-activated $^{3}$-particle scintillation counter</td>
<td>Ra de-emanated into scintillation chamber after 30 days ingrowth. Counting begun 4.5 h after transfer</td>
<td></td>
</tr>
<tr>
<td>Kahlos and Asikkainen (1975)</td>
<td>Assay of natural radioactivity in sea water</td>
<td>600 to 800 l</td>
<td>Acidify with HCl, add Fe and Ba carriers, $^{208}$Pb tracer, ppt. Fe(OH)$_3$ and Ba(BaSO$_4$ with NH$_4$OH)</td>
<td>Hydroxides dissolved in HCl, sulfates transferred to carbonates, dissolved in HCl</td>
<td>None</td>
<td>Nothing</td>
<td>Ra de-emanated into scintillation chamber after 30 days ingrowth. Counting begun 4.5 h after transfer</td>
<td></td>
</tr>
<tr>
<td>Kaufman et al. (1973), Broecker et al. (1973)</td>
<td>Assay of natural radioactivity in sea water</td>
<td>20 l, 1 to 5 g sediment</td>
<td>Add Pb carrier, $^{208}$Pb tracer, Sediment: ignite and leach with HCl</td>
<td>Water: coppt. on AlP$_2$O$_5$, dissolve in 4 M HNO$_3$; Sediment: coppt. on Pb(NO$_3$)$_2$ with 75% HNO$_3$</td>
<td>Separate Ra and Pb on anion exchange column, alkaline earths on cation exchange column</td>
<td>Electroplated on Pt planchet after at least two weeks wait for $^{210}$Pb to decay</td>
<td>Ra de-emanated into scintillator cell</td>
<td></td>
</tr>
<tr>
<td>Kilde and Hvidland (1975)</td>
<td>Assay of natural radioactivity in drinking water</td>
<td>1 liter</td>
<td>Add citric acid, Pb, Ba and Y carriers, heat</td>
<td>Add NH$_4$OH, ppt. mixed sulfates with H$_2$SO$_4$, then add (NH$_4$)$_2$SO$_4$</td>
<td>Multiple coppt. on Ba(NO$_3$)$_2$ and on BaSO$_4$</td>
<td>In alkaline EDTA-solution, or in BaSO$_4$ ppt. on stainless steel planchet</td>
<td>$^{228}$Ra tracer, Ac &quot;cow&quot; is required</td>
<td>$^{3}$-spectrometry with semiconductor detector</td>
</tr>
<tr>
<td>Kuchta et al. (1976)</td>
<td>Assay of skeletal $^{228}$Ra and $^{228}$Th in presence of gross amounts of $^{228}$Ra in bone samples</td>
<td>Not specified</td>
<td>Dry ash sample, dissolve ash in HNO$_3$</td>
<td>None</td>
<td>None</td>
<td>Nothing</td>
<td>Ra de-emanated into scintillator cell</td>
<td></td>
</tr>
<tr>
<td>Special Items</td>
<td>Purification</td>
<td>Final Form</td>
<td>Yielded By</td>
<td>Waiting Period</td>
<td>Counted By</td>
<td>Special Items</td>
<td>Comments</td>
<td></td>
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</tr>
<tr>
<td>Heated ion exchange columns (60°C)</td>
<td>Liquid-liquid extractions using TTA in benzene; ion exchange columns</td>
<td>La(Ac) oxalate.</td>
<td>Not mentioned, but could be gravimetrically</td>
<td>None stated, but sample should be</td>
<td>G-M tube or proportional counter, with absorber when</td>
<td>None</td>
<td>Sekine et al. (1967) say TTA equimolar with TBP in</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2nd ion exchange column at 60°C. Ac eluted with 6 M HNO₃, Ac copptd. on Fe(OH)₃, impurities scavenged on Pb and 81 sulfides</td>
<td>solution evap. on stainless steel planchet</td>
<td></td>
<td>sample should be</td>
<td>228Ac ingrowth</td>
<td></td>
<td>TTA is superior to TTA only</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe(AC)(OH)₃ dissolved in HNO₃, known fraction evaporated on planchet</td>
<td>Weighings of ppt. containing Ra and Ac, or spectrophotometric assay of Fe</td>
<td></td>
<td>Gas-flow proportional counter with 13 mg/cm² absorber</td>
<td></td>
<td>Ba initially present in samples. Na, K, Ca, Mg, and Al each more than 100 ng/g in typical samples</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ppt. Ce with HNO₃, dissolved ppt. in HNO₃, add 8a holdback carrier, reppt. Ac on Ce(OH)₃,</td>
<td>Evap. acid solution to dryness on 5-cm diameter planchet</td>
<td></td>
<td>228Ac ingrowth</td>
<td></td>
<td>Method not tried on very low activity samples</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Th purified on cation and anion exchange columns, extracted into TTA in benzene, evaporated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Method could be changed to assay 222Ra first. No specifics given for assaying biologicals. Section 11 wrongly states no 222Ra std. are available</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>On sage planchet as 228Ra</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>226Ra could be counted by de-emanation of 222Rn</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>See under 226Ra; none additional</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Method is based in part on Moore (1969a). Kauss et al. (1978) found precision of assays better by counting 229Th than by counting 228Ac.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>As for 226Ra plus copptn. of ingrown Ac on Y(Oh)₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>226Ra/228Ra activity ratio must be at least 0.1. As check, ingrown 222Rn can be counted later. Cochran (1974) completely dissolved sediments.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>None except by Rn de-emanation using a flow-through collection chamber</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Chemical yield of Ac is incorrectly calculated—see text</td>
<td></td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Reference</th>
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<th>Yielded By</th>
<th>Counted By</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mackenzie et al. (1974)</td>
<td>Assay of 226Ra and other radio-nuclides in sea water and marine sediments</td>
<td>226Ra and 228Ra in drinking water</td>
<td>Water: 10 to 20 l for 226Ra; 50 l for 228Ra, Sediment: 5 to 10 g</td>
<td>226Ra: none, 228Ra: absorb on MnO(2), desorb with HCl, coppt. on BaSO4</td>
<td>Dissolve ppt. in alkaline EDTA solution, reppt. BaSO4 with acetic acid</td>
<td>222Ra in gas</td>
<td>Nothing, but analysts say assay is quantitative</td>
<td>( \alpha ) -scintillation in modified Lucas cell</td>
</tr>
<tr>
<td>McConkey and Sellar (1979)</td>
<td>Assay of 226Ra and 228Ra in ground waters</td>
<td>226Ra: 0.8 l, 228Ra: 10 to 20 l</td>
<td>None (waters assayed were clear)</td>
<td>226Ra: none, 228Ra: absorb on MnO(2), impregnated acrylic filters, coppt. with HCl, ppt. on BaSO4</td>
<td>Add acetic acid, coppt. Ra with BaCl2, on BaSO4, Dissolve ppt. in DTPA solution</td>
<td>222Ra in gas</td>
<td>Nothing, but each sample run at least twice</td>
<td>( \alpha ) -scintillation chamber</td>
</tr>
<tr>
<td>Michel and Moore (1980)</td>
<td>Assay of 226Ra and 228Ra in soils, waters, ores, and mill tailings and effluents</td>
<td>5 g of solids, 0.1 to 1 liter of liquid</td>
<td>Liquids: acidify, wait overnight, coppt. on PbSO4, do sulfate fusion</td>
<td>226Ra: none, 228Ra: absorb on MnO(2), impregnated acrylic filters, coppt. with HCl, ppt. on BaSO4</td>
<td>Add acetic acid, coppt. Ra with BaCl2, on BaSO4, Dissolve ppt. in DTPA solution</td>
<td>222Ra in gas</td>
<td>Nothing, but each sample run at least twice</td>
<td>( \alpha ) -scintillation chamber</td>
</tr>
<tr>
<td>Percival and Martin (1974)</td>
<td>Assay of 226Ra and 228Ra in biological and mineral samples</td>
<td>Up to 50 g of bone ash, up to 20 g of food or plant soil; 5 g of minerals</td>
<td>Minerals: Fuse with Na2CO3, digest in HNO3. All types: dissolve in acid</td>
<td>226Ra: none, 228Ra: absorb on MnO(2), impregnated acrylic filters, coppt. with HCl, ppt. on BaSO4</td>
<td>Liquid-liquid extractions with Alkaptop 336 and DEHPA to remove Th. Coppt. Ra on PbSO4</td>
<td>222Ra in gas</td>
<td>Pulse-ionization chamber or ( \alpha ) -scintillation cell</td>
<td></td>
</tr>
<tr>
<td>Petrow et al. (1964)</td>
<td>Assay of 226Ra and 228Ra in sea sediments</td>
<td>228Ra in sea water and 226Ra in sea sediments</td>
<td>80 l</td>
<td>228Ra: BaCl2 and FeCl2, add H2O, ppt. Fe(0H)3 and BaSO4 ppt.</td>
<td>Cation exchange separation of Ra and Ba, Ra coppt. on Pb(NO3)2, separated by knip exchange at 60°</td>
<td>Electrowpated on stainless steel planchet</td>
<td>222Ra for dissocation only, 228Ra for entire assay, from (^{222}Rn) &quot;cow&quot;</td>
<td>( \alpha ) -spectrometry with Frisch-grid pulse- ionization chamber</td>
</tr>
<tr>
<td>Sakanoue et al. (1973)</td>
<td>Assay of 226Ra in sea water and 226Ra in sea sediments</td>
<td>226Ra in sea water and 226Ra in sea sediments</td>
<td>Up to 10 g of plant ash and soil</td>
<td>226Ra: Repeated evap. with HClO4 and HF, dissolve residue in HCl</td>
<td>Cooppt. Ra on Ba and Pb sulfates, Ppt. dissolved in alkaline EDTA, sulfates reppt. with acetic acid</td>
<td>Ba(252)SO4 ppt. dispersed in toluene containing PPO, POPOP, and colloidal silica</td>
<td>Nothing, but each sample run at least twice</td>
<td>Liquid-scintillation, two counts several weeks apart</td>
</tr>
<tr>
<td>Smith and Mercer (1970)</td>
<td>Assay of 226Ra and 228Ra in soils and plants</td>
<td>Up to 10 g of plant ash and soil</td>
<td>Repeated evap. with HClO4 and HF, dissolve residue in HCl</td>
<td>226Ra: Repeated evap. with HClO4 and HF, dissolve residue in HCl</td>
<td>Cooppt. Ra on Ba and Pb sulfates, Ppt. dissolved in alkaline EDTA, sulfates reppt. with acetic acid</td>
<td>222Ra in gas</td>
<td>Nothing, but each sample run at least twice</td>
<td>( \alpha ) -scintillation chamber</td>
</tr>
<tr>
<td>Tonta (1971)</td>
<td>Assay of low Ra concentrations in mineralized waters</td>
<td>10 l</td>
<td>Add citric acid and NaOH, then Pb and Ba carriers</td>
<td>Mixed ppt. with H2SO4</td>
<td>Cation exchange separation of Ra and Ba, Ra coppt. on Pb(NO3)2, separated by knip exchange at 60°</td>
<td>Ba(252)SO4 ppt. dispersed in toluene containing PPO, POPOP, and colloidal silica</td>
<td>Nothing, but each sample run at least twice</td>
<td>( \alpha )-scintillation chamber</td>
</tr>
</tbody>
</table>

**ABBREVIATIONS:**
- \( p \) = particle
- \( \alpha \) = particle
- coppt. = coprecipitate
- DEHPA = bis(2-ethylhexyl)phosphoric acid
- DTPA = sodium diethylenetriaminopenta acetic acid
- EDTA = sodium ethylenediaminetetraacetate
- evap. = evaporate, evaporated
- G-M = Geiger-Muller
- PMA = pulse height analyzer
- PPO = 1,4-di-((2-(5-phehnyloxazoyl))benzene
- PPD = 2,6-diphenyloxazole
- ppt. = precipitate (as verb and as noun)
<table>
<thead>
<tr>
<th>Special Items</th>
<th>Purification</th>
<th>Final Form</th>
<th>Yields By</th>
<th>Waiting Period</th>
<th>Counted By</th>
<th>Special Items</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-liter glass vessel</td>
<td>Sr removal step: extractions of Sr by TTA in benzene; store 5 weeks; none extractions of Sr</td>
<td>Evap. organic phases on heated stainless steel planchet</td>
<td>Same as 226Ra</td>
<td>12 d for 226Ra ingrowth, at least 5 weeks for decay of 226Th progeny</td>
<td>Tracerlab Omniguard (gas-flow GM counter with anticoincidence)</td>
<td>MnO₂-impregnated acrylic fibers, Pt crucible</td>
<td>Method does not discuss assay of 226Ra in sediments</td>
</tr>
<tr>
<td>4 timer SCA, 2 coincidence analyzers, special detector assembly, PFA</td>
<td>Apparently none. See under 226Ra</td>
<td>Same as 226Ra</td>
<td>2 d counting of 226Ra</td>
<td>As for 226Ra</td>
<td></td>
<td></td>
<td>Considerable instrumentation is required, but amount of radiochemistry is reduced</td>
</tr>
<tr>
<td>Pt dish</td>
<td>Carbonate fusion, dissolve mixed ppt. in HCl, co-</td>
<td>Purify Th by ion exchange, mount on planchet for thinnest source of counting</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ra extraction by fibers based on Krishnaswami et al. (1973) and on Moore and Reid (1973)</td>
</tr>
<tr>
<td>None</td>
<td>Pt dish</td>
<td>Evap. final acid solution on 5-cm diameter stainless steel planchet</td>
<td>Nothing</td>
<td>At least 20 h for 226Ac ingrowth</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>None</td>
<td>Evap. on stainless steel plate</td>
<td>226Ra assay on initial sample and on Ra (RaCl₂) solution just before AC extraction. Extraction is not yielded</td>
<td></td>
<td></td>
<td></td>
<td>This method is a variation of similar method by Petrow and Allen (1961) for U mill effluents which also is unyielded</td>
</tr>
<tr>
<td>None</td>
<td>None</td>
<td>Solution evap. on stainless steel planchet</td>
<td>7 to 10 d for growth of 226Ac</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>None</td>
<td>Evap. on stainless steel plate</td>
<td>Equilibrium between 226Ra and 226Th assumed. If not so, must reextract several months later</td>
<td></td>
<td></td>
<td></td>
<td>Use of moderately complex equations of ingrowth and decay is required</td>
</tr>
</tbody>
</table>

rept. = reprecipitate  
SCA = single channel analyzer  
std. = standard  
TBP = tributylphosphate  
TFA = 2-thiolytrifluoroacetone
Evaluation of Methods for the Assay of $^{228}$Ra in Water

J.R. Noyce

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Las Vegas, NV 89118

The technical literature from 1967 to May 1980 was searched for methods for assaying radium-228 in water. These methods were evaluated for their suitability as potential EPA reference methods for drinking water assays. We suggest the present EPA reference method (Krieger, 1976) be retained but improved, and a second method (McCurdy and Mellor, 1979), which employs $\beta$-$\gamma$ coincidence counting, be added. Included in this report is a table that lists the principal features of 17 methods for radium-228 assays.

Analysis; assay; evaluation; radioactivity; radiochemistry; radium-228; reference method; water.

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